Corrosion in Biomedical Grade Titanium Based Materials: A Review

KEYWORDS Corrosion, Biomedical Titanium Alloys, Microstructures Features, Heat Treatments

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ABSTRACT *Apart from ceramics, polymers, and composites, metallic materials rank distinguished in the field of biomaterials. Recently, titanium based materials are attracting much interest as implantable materials because of their superior corrosion resistance, superior mechanical properties such as remarkably high specific strength, low elastic modulus, and the greatest biocompatibility compared to other competing biomaterials like stainless steel, Co-Cr alloys and nitinol alloys. Implantable Ti based materials must have high corrosion resistance to withstand the degradation which results from the reactions with the hostile body environment and does not result in adverse biological troubles in the body. At the same time, Ti materials must be stable and retain their properties for a long time reliably. This review discusses the important of Ti based materials as biomaterials from the point of view of corrosion science. The present article discusses various issues associated with biological corrosion of various categories of Ti materials which can be of use in different areas of clinical applications. The importance of creation of stable, compact and continuous oxide layers on the surface of Ti materials has been strongly effective to combat corrosion in aggressive body fluid. In this review, extensive efforts have been made to accumulate the effect of thermal and thermomechanical processing on corrosion resistance of biomedical titanium alloys. This paper concentrates its interest mainly on the evolution, evaluation and development of effective microstructural features that can improve corrosion properties of bio grade titanium materials via using thermal and thermomechanical treatments.*

INTRODUCTION

The application of biomaterials in the ancient times has been practiced more as an art and entirely lacked in terms of scientific knowledge until advanced attempts from researchers and scientist were made recently to develop this field of engineering medical sciences. Of late, the research on biomaterials has gathered significant interest as these materials are extensively used to fix and replace decayed or damaged parts of the human systems such as heart valves, bones, joints and teeth, etc. The research on biomaterials initially started by testing of these materials on animals and their acceptability on the human body system were indirectly established. Biomaterials have been defined as any substance (other than a drug) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or as a part of a system which treats, augments, or replaces any tissue, organ, or function of the body [1]. Nowadays, the mainly familiar kinds of materials used in biomedical applications are Metals, Ceramics, Polymers, and Composites. It is well known that prosthetic devices and components need to fulfil several imperative requirements so that they are successful in service over a long-term usage in the body without rejection and minimal failure. Titanium has been commercially offered during last more than 60 years and since then several titanium based materials have been developed as a surgical material until 1960. However, mid 1970s, has witnessed path-breaking developments in the advancements on Ti based biomaterials have been increasing gradually [2-4].Titanium and its alloys , so far, have proved to be the most befitting materials for biomedical applications due to their particular characteristics such as better mechanical properties, excellent biocompatibility and superior corrosion behaviour [5]. There exists, yet, an inevitable fact that nearly all metallic materials electrochemically corrode to some degree when they come in contact with hostile/aggressive fluid under certain conditions. Therefore, corrosion in two forms, general and localized, is one of the main problems of metallic biomaterials. Consequently, it has become the most important parameter when it comes to choosing the materials for surgical implants in hostile solutions which simulate the media of the human body. Degradation of material and released ions are the most common consequence of reaction between body fluids and implant which result in several problems including inflammation, formation of foreign body giant cells [6], and may cause loosening of implant from the bone [7] due to osteolysis [8]. The health facts of such nature have been widely reported in the literature [9-10]. The researchers reported that release of metal ions adversely effects the healing of bone and the surrounding tissues. In addition, corrosion of the implant itself is bound to affect the essential properties of the implant such as fatigue life and tensile strength leading to the poor mechanical compatibility and eventually may result in inevitable failure of the implants [11]. Hence, controlling and protection of an implant material from corrosion are basic and indispensable demands. Thermal and thermo-mechanical treatment (TMT) are paramount techniques that can achieve and control the desired microstructure by altering the transformation mechanisms of size, volume fraction, arrangement, and shape of the two main phases α and β that describe the microstructure, and other phases present in Ti alloys. It is well known that the material's microstructure has a great effect on the corrosion characteristics of biomedical Ti based materials. It is, therefore, very important to know the kinetics of parameters affecting the phase transformations during different heat treatments and thermo-mechanical regimes, which would allow optimization of processing parameters (temperature, time, cooling rate, and plastic deformation parameters) in order to provide optimum corrosion behavior by desired microstructure.

Taking cues from the essence of corrosion behaviour of biomedical alloys extensive research is being done to understand foremost forms of corrosion and their influence that titanium materials commonly experience and their implications on biological functions. The importance of the subject, increasing research interest and huge unexplored potential is the driving force behind this literature review. The present review study has been done with a view to provide the researchers in the field to have a bird's eye view on the hotspots on research in the corrosion behaviour of biomedical grade Ti alloys.

OVERVIEW OF BIOIMPLANT TITANIUM BASED MATERIALS SYSTEMS

Ti based structural materials may be classified as Alpha (α), near-α, Alpha-Beta (α-β), metastable β and stable β depending on the microstructure at room temperature. In this regard, alloying elements for Ti fall into three categories: (1) α-stabilizers, such as Al, O, N, C; (2) β-stabilizers, such as V, Nb, Ta, Mo (isomorphous), Fe, W, Cr, Ni, Si, Co, Mn, H (eutectoid); (3) neutrals, such as Zr and Sn [12]. The α and near-α Ti alloys exhibit superior corrosion resistance but have limited low temperature strength. In contrast, α + β alloys exhibit higher strength due to the presence of both α and β phases. The β alloys also offer the unique characteristics of low elastic modulus and superior corrosion resistance [13-14]. Among diverse titanium materials, earlier systems of Ti in medical, surgical and dental devices were based on commercially pure Ti (cpTi) and most popularly used Ti-6Al-4V alloy. These two Ti based materials account for the major market share for biomedical applications and has become standard biomedical materials. Due to the fact that releasing small amounts of V and Al in the human body induces possible cytotoxic effects and neurological disorders, respectively [15-18] led to the development of Ti-6Al-7Nb [16], Ti-Zr based and Ti-Sn based alloys [19] with mechanical properties comparable to those of high strength alloy Ti6Al4V and better corrosion resistance.

The β stabilizers are considered as superior biocompatible elements since they induce many attractive properties like low elastic modulus, a design of Ti alloys with Nb, Zr, Mo, Ta etc. consequently these alloys have gained great attention in recent years. Hence, corrosion properties of non-toxic β-type Ti alloyed systems have been developed recently such as: Ti-Nb system, Ti-Nb-Zr system, Ti-Nb-Sn system, Ti-Nb-Zr-Sn system, Ti-Nb-Ta-Zr system, Ti-Nb-Zr-Ta system, Ti-Zr-Ta-Nb system, Ti-Mo system, Ti-Mo-Zr system, Ti-Mo-Nb, Ti-Mo-Nb-Zr-Sn system, Ti-Cr-Nb system alloys [20-34] and several other systems are still evolving. For instance, several studies have shown that titanium alloyed with molybdenum possesses better electrochemical behavior than pure titanium [35–38]. In particular, Oliviera and Guastaldi [35] have investigated Ti–Mo alloys with different Mo content and found that alloy with 15 wt% Mo has better corrosion behavior in chloride environment compared to other Mo concentrations. Also, a study on new titanium-based alloys including Ti-10Cr-20Nb, Ti-20Cr-10Nb and Ti-20Cr-20Nb was conducted to develop adequate microstructure and properties for biomedical applications. The results reported an excellence corrosion resistance and very similar and high pitting potential values were achieved as a result of a very good stability of the passive oxide film [34].

CORROSION IN METALLIC BIO-IMPLANTS

Corrosion is one of the main processes that cause gradual degradation of metals by electrochemical reactions when a metallic bio-implant is placed in the hostile aqueous medium comprising of human body fluids. It is pertinent to mention here that in order to mitigate the effects of corrosion and related problems a comprehensive and most up-to-date understanding of the important principles governing corrosion behaviour of implantable materials is highly essential. When the foreign material is implanted in the human body it encounters hostile corrosive environment comprising of various body media such as blood, water, sodium, chlorine, proteins, plasma, amino acids and mucin in saliva [39]. Generally, the electrochemical reactions that occur on the surface of the implants are akin to reaction in seawater. The human body fluid consists of diverse constituents such as anions (chloride, phosphate, and bicarbonate ions), cations (Na^+, K^+, Ca^{2+}, Mg^{2+} etc.), organic substances with two types: low-molecular-weight species in addition to those with relatively high molecular-weight, and dissolved oxygen [40, 41]. Researchers have investigated the corrosion behavior of Ti and its alloys using certain types of biological media [42-44]. Corrosion studies on orthopaedic biomaterials have been frequently carried out in Hank's solution, Ringer's solution, and artificial saliva.

The makeup of the body solution is highly transient with time and more importantly with variations in the dietary intake. This causes fluctuation in the prevalent equilibrium conditions due to variation in the cation and anion reactions consequently making the corrosion behaviour of the implants in human body solutions highly complex. The equilibrium conditions get destroyed across the surface double layer which is created by the electrons on the surface. Additionally, the amount of excess cations present in the solution via proteins carries the metal ions away from the implant surface. Moreover, absorbed proteins on the surface can decrease the diffusion of oxygen at specific areas and cause favoured corrosion in those areas. It has been found that bacteria present in the body fluid may absorb the hydrogen produced due to cathodic reactions in the surrounding area of the implant. The hydrogen, since it plays a positive role as an inhibitor element, depletes from these regions and in turn affects the corrosion behaviour in terms of enhanced corrosion factor. It is noticed that the pH values of human body environment change from the normal value at 7.0 to more at 9.0 or less at 3.0 owing to numerous reasons that induce imponderables in the entire biological system such as diseases, infections, accidents and others. Currently, it is well known from medical studies that corrosion in implants is an inevitable process in spite of protective films on its surface. Even though advanced efforts are constantly introduced to develop the improved implant materials, clinical evidences reveal that these new materials are also susceptible to corrosion to a particular level [47]. Also, corrosion is responsible for the release of metal ions from the implants which in turn cause discoloration of adjacent soft tissues and allergic problems. However, corrosion rate of metallic implant systems must not exceed the acceptable rate which is about 0.00025 mm/yr, or 0.01 mils/yr [48]. The two physical features that determine corrosion mechanisms in implants are thermodynamic forces which correspond to the energy required or released during oxidation or reduction reactions and the kinetic barriers such as surface oxide film which physically impede corrosion reactions [49-50]. The corrosion of implants is closely related to other resultant processes such as wear and fretting leading to tribo-corrosion and the implant in this case will not fail immediately due to corrosion. Wear and fretting processes contribute a lot to the damage of protective surface oxide films, creation of cracks and split of reactive metal atoms on the surface that are prone to corrosion [51]. For an enhancing corrosion resistance, it is necessarily that the surface passive film must be non-porous, its atomic structure is averse to migration of ions and electrons across the metal oxide-solution interface. To fulfil the biomedical engineering requirements, the corrosion behaviour of the implants, depending on their application, should be tested under different possible conditions such as wear, fretting, fatigue, stress corrosion etc. The ASTM standards are available to evaluate and test corrosion resistance of implant materials under different conditions. The frequently used standards for testing various corrosion processes are given in Table 1.

Table 1. Standards for Testing Corrosion Resistance of Biomaterials [52]

ASTM Standards	Specifications
ASTM G 61-86,and ASTM G 5-94	Corrosion performance of metallic biomaterials
ASTM G71-81	Galvanic corrosion in electrolytes
ASTM F746-87	Pitting or crevice corrosion of metallic surgical implant materials
ASTM F2129-01	Cyclic potentiodynamic polarization measurements

INFLUENCE OF CORROSION ON BIOCOMPATIBILITY

Biocompatibility is the most important prerequisite for any biomaterial since it ultimately affects the performance of implant device. In general, the term "biocompatibility" is defined as simply as the ability of a material to be accepted by the human body. In other words, biocompatibility is the state of mutual coexistence between the biomaterials and the biological environment such that neither has an undesirable effect on the other. Because all materials generate a "foreign body reaction" when implanted in the body, the degree of biocompatibility is related to the extent of this reaction. Hence, biocompatibility is directly related to the corrosion behavior of the material and its tendency to release potential toxic ions [53]. Alternatively, corrosion weakens the implants and in turn results in an early failure and may cause tissue reactions which lead to the release of corrosion products from the implants. The vivo studies related to the implantation of the devices have revealed that the concentration of various ions is significantly higher close to the tissues. Thus, once a foreign material is implanted, the body may react unfavourably in several ways. The factors that determine the interactions between the biomaterial and the tissues are of prime significance whether these factors have chemical and/or mechanical mechanisms. It is clear that any adverse host tissue reaction with the implant can lead to an inevitable device failure. The presence of the implant may possibly inhibit the defence mechanisms of the human body leading to infection, chronic inflammation necessitating the removal of the implant [54]. Typically, chronic inflammation and/or hypersensitivity are undesirable outcomes from these reactions. Hypersensitivity depends basically on the cell's contact with the metallic ions or salts and it affects to a large extent on the life of more than 15% population [55,56]. Also, corrosion products as metal ions may play an important role to adversely affect health related problems such as cytotoxicity, genotoxicity, carcinogenicity, etc.

EFFECT THE MICROSTRUCTURAL FEATURES ON CORROSION RESISTANCE OF BIO GRADE TITANIUM ALLOYS

Several studies on biological behavior of metallic implants revealed that the composition and microstructure features of biomaterials must be carefully tailored to contain the adverse body reactions. The influence of microstructural features on corrosion characteristics of biomedical Ti alloys is extensively explained by Dull et al. [57]. They reported that the passive corrosion current density increases with ratio of α to β transformation as a result of creation a galvanic cell between two phases of (α+β)Ti–6Al–4V alloy due to β and α stabilizers V, and Al respectively. The type of microstructure has considerable effect on corrosion properties as reported by Raja et al. [58]. They revealed that Widmanstatten structure resulted from β solution treatment on Ti–6Al–2Sn alloy has high corrosion rate due to variations of composition within the structure. Geetha et al. [59] studied the corrosion behaviour of heat-treated Ti–13Nb–13Zr alloy, and the spontaneous passivity of solution treated and solution treated plus aged specimens was found irrespective of the cooling conditions. All the air-cooled samples exhibited active open circuit polarization (OCP) and high passive current density as compared to the water quenching (WQ) and furnace cooling (FC) samples. They established that equiaxed microstructure is preferred for biomedical applications, when this microstructure has given noble OCP and low passive current density. They also showed the effect of aging heat treatment on the formation of a stable protective oxide layer in the surface of (α + β) ST/WQ samples by distribution of the alloying elements in the phases developed during the heat treatment. Adding aging treatment after solution treatment considerably affects corrosion properties as pointed out by Yu and Scully [60]. They studied β ST Ti–15Mo–3Nb–3Al and compared its microstructure with age hardened condition. They found that β solution treated microstructure seems higher corrosion resistance than aged alloy because of the partitioning of the alloying elements during aging process [61]. Moreover, the research on thermal and thermomechanical processing shows that the type of cooling media also plays an important role on corrosion behavior . Majumdar et al. [23] performed rolling at 800◦C and 650◦C (above and below β transus temperature) followed by solution treatment at 800 ◦C, 700 ◦C and 650 ◦C for 1 h in dynamic argon atmosphere with various cooling media furnace cooling, air cooling, and water quenching. They have found that the microstructure of the heat treated TZN alloy mainly consisted of elongated/equiaxed α, β or martensite. The furnace cooled TZN samples showed lower corrosion potential (Ecorr) than the air cooled samples. Also, an aging heat treatment after solutioning of water quenched samples was found to decrease the Ecorr value. Cremasco et al. [20] performed thermomechanical processing on β Ti–35wt%Nb alloy by solution treating at 1000◦C for 24 h (within the β range) followed by hot working at 800◦C, then heat treating again at 1000◦C for 1 h and cooling under two different cooling conditions: WQ and FC. Both cooling media reported to have provided a passive film formation during corrosion tests in 0.9% NaCl. The film formation was observed with very low experimental current densities, and after second polarization cycle the corrosion rates were found to decrease due to formation of a thicker titanium oxide layer. Further, the corrosion tests revealed that the electrochemical corrosion resistance of WQ samples were less as compared to that of the FC samples due to stress-induced martensitic transformation. Zhoua et al.[29] investigated the effect of cold rolling and solution treatment above β transus temperature on the corrosion resistance of two medical Ti alloys (α+β) Ti–10Mo and βTi–20Mo. The results have revealed that both of the Ti–Mo alloys cold rolled and solution treated exhibited a passive behavior in 5% HCl, which was found to be attributed to the passive film formation of a mixture of MoO_3 and TiO_2. Further, the cold rolling process did not influence the formation of passive films on the Ti–Mo alloys although it slightly increases the passive current densities. Both Ti–Mo alloys exhibited better corrosion resistance than CP Ti and their corrosion resistance increased with increasing Mo content. According to Zhao et al [30], solution treated (at 1133 K plus water quenching) β metastable Ti–12Mo–5Zr alloy exhibited good resistance to corrosion as compared to Ti–6Al–4V alloy. The attributed the results to the formations of equiaxial β phase (the nobler phase) microstructure without precipitation of α" martensite phase (the less noble acicular phase) which prevents galvanic effect. Cvijovic´-Alagic´ et al. [22] investigated the corrosion behaviour of solution treated (in the β region i.e. heating in 900◦C for 30 min followed by water quenching) and 25% cold rolled, martensitic Ti– 13Nb–13Zr alloy and heat treated Ti–6Al–4V ELI alloy in martensitic phase and non martensitic phase with (α+β) by studying the microstructures in Ringer's solution. They demonstrated that the alloys exhibited spontaneous passivity but martensitic Ti–13Nb–13Zr and martensitic Ti–6Al–4V ELI alloys showed improved corrosion resistance compared to (α+ β) Ti–6Al–4V ELI alloy mainly due to the formation of a hard martensitic microstructure.

Several efforts are directed towards refining the structure of medical Ti and its alloys by different methods. Thermomechanical processing is one such treatment which can be performed by newer techniques (which was discovered in 1991) such as friction stir processing (FSP) and friction stir welding (FSW) [62]. During surface treatment by FSP ultra-fine grain microstructure is formed on a macro scale which leads to substantial changes in the size, spatial distribution, composition of α and β phases and improvement of various properties of medical titanium alloys [63,64]. To evaluate the effect of FSP created microstructures of the Ti alloys, Atapour et al. [65] investigated the corrosion behaviour of investment cast Ti-6Al–4V. They studied the microstructure before and after FSP above and below the β transus in deaerated 5% HCl at room temperature. They found that the grain size, microstructural morphology and elemental partitioning are the main factors which controlled the corrosion behavior of the friction stir processed samples. They noticed that untreated base metal and both friction stir processed conditions (above and below the β transus) exhibited active–passive behaviour. Corrosion tests showed that samples processed below the β transus exhibited shorter activation time at open circuit and higher corrosion rate than the base metal than the samples processed above the β transus. Scanning electron microscopy performed by them revealed that for 50 h immersion in 20% HCl at 35°C the β phase was preferentially dissolved from the base metal, probably as a result of the higher V content relative to the α phase. Also, the transition zone of samples processed below β transus exhibited more attack than the samples processed above β transus. The researchers attributed this improvement in the corrosion resistance to large β volume fraction as well as coarsening of β phase. Moreover, samples from the stir zone which were processed below β transus exhibited much more severe attack compared to that of the samples processed above β transus which they concluded to be due to a preferential attack on α phase.

The importance of thermomechanical processing on the corrosion resistance of biomedical Ti alloys has corroborated by Vasilescu et al. [28] on Ti–10Zr–5Ta–5Nb alloy in physiological fluids of different pH values. They thermomechanically processed the alloys by plastic deformation (almost 90%) using rolling at 1000°C in 16 steps accompanied by an initial heat treatment (heating at 1000°C for 2 h followed by WQ) and final heat treatment (heating at 1000°C for 1 h followed by FC). They reported that the alloy showed self-passivation, with a large passive potential range and low passive current densities, namely, a very good anticorrosive resistance in Ringer's solution of acid, neutral and alkaline pH values. However, the best behavior was noticed in neutral Ringer's solution. They also pointed out the importance of the thermomechanical treatment and its influence on corrosion behaviour as their results indicated an improvement of all electrochemical parameters and of the corrosion rates in comparison with the untreated alloy.

Among thermal treatments, laser process, such as laser metal deposition (LMD), selective laser melting (SLM) or laser remelting (LR) are being currently employed to achieve outstanding properties. Recently, there is a great attention to LR treatments as this process provides many advantages such as high processing rates, limiting the risk of oxidation [66], refined microstructure, reduced microsegregation, extended solid solubility and ability to form metastable phases [67-68]. Amaya-Vazquez et al. [69] applied LR treatment with a high power diode laser, on two titanium alloys (TiG2 and Ti6Al4V). The results for TiG2 samples showed that the treatments did not alter the corrosion resistance significantly, probably because the alloy did not undergo phase transformations. On the contrary, during LR treatment of Ti6Al4V samples they observed two distinct patterns: (i) at high fluences (F between 10 and 30 kJ/cm^2) only two zones were present (MZ and HAZ) and (ii) at low and medium fluencies (F between 0.5 and 10 kJ/cm^2), three zones are present (MZ, HAZ and BM). At high fluences, laminar α+β microstructure was formed in the MZ, while at low and medium fluencies the microstructure consisted of α′ martensite. Low fluences (F lower than 1 kJ/cm^2) led to very thin martensitic layers. The martensitic microstructure showed a significant increase in microhardness and an improved corrosion resistance as compared to the other microstructures.

CONCLUSIONS

The field of biomedical materials plays a significant role in manufacturing of a variety of biological artificial replacements which are very common in the modern times. Among bioimplanable metals, titanium and its alloys offer the best corrosion resistance compared to other competing materials such as Cr–Co, Ni–Ti, and SS316L alloys. Moreover, Titanium and its alloys are the materials of choice in biomedical devices and components since long time, as these materials posses superior properties and performance especially biocompatibility and corrosion behaviour. Despite its ever increasing application, the potential of titanium alloys still remains under exploited in this vital field. Corrosion is the first and foremost consideration for a material of any kind that is to be used in the body due to the corrosive nature of the body fluid. Its effect is unavoidable causing release of metal ions which affect the health adversely. Corrosion can reduce the life span of implanted device and consequently may impose revision surgery. In addition, the human life may be endangered due to ill-effect of corrosion. The biocompatibility of Ti alloys is seriously affected by the as corrosion results in the release of undesirable ions from these materials. Even though Ti materials are characterized with spontaneously formation of protective uniform and adherent oxide film, their corrosion in simulated body fluid with releasing ions can cause serious health problems in bio-applications. Great efforts have been performed to replace the toxic constituents and create new kinds of Ti alloys from biocompatible β stabilizing elements such as Nb, Mo, Zr, Ta, etc. The literature reveals that serious attempts have been made from researchers towards understanding the technology by way of structure-property co-relation to uncover the new facets of titanium and its unique characteristics that will improve function and lifetime of an implant in the human body. Thermal and thermomechanical treatments are important technniques which are used by researchers for designing and optimizing various properties of medical titanium materials including corrosion via control of alloy composition, varieties of phase fractions, their morphologies and precipitations in the microstructure. It is inferred from the literature, that up to this day, an ideal combination of corrosion properties is still a challenge as far as the application of Ti based materials is concerned in the biomedical field. Therefore, classified literature presented in this paper is expected to confer a road map for an interdisciplinary approach in the design and control of desirable corrosion properties of biomedical titanium materials. This is also expected to encourage researchers to continue performing focused studies in the entire gamut of corrosion behaviour of biomedical titanium alloys and its alleviation by different methods and techniques.

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